

## **DEGRADABLE AND HYDROLYZABLE BINDER EXPLOSIVES**

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### **ABSTRACT**

High explosives cast in military hardware are generally prepared to meet the demands of rough handling, as well as long-term storage. At some point, however, if the ordnance items that contain them are not detonated as intended, the explosives lose their effectiveness and reliability. Excessive aging, deterioration, or some other unanticipated event will require their safe disposal.

Air pollution abatement and environmental control regulations have now imposed constraints on methods of disposal and demilitarization of unserviceable ordnance explosives. An attractive alternative to continued open burning and demolition would be the development of a cast explosive whose main constituents could be degraded and recycled into reusable explosive solids and liquid by-products which are environmentally non-hazardous.

Past research and technology work at the Naval Air Warfare Center Weapons Division, China Lake, Calif., has culminated in the successful development of a castable plastic-bonded explosive composition that has the following desirable characteristics: (1) it is water degradable and leaves no toxic products behind; (2) it contains a binder which hydrolyzes but does not form a highly viscous gel; (3) it contains a binder which does not degrade in the presence of water alone; and (4) it produces an acceptable energy output level as a main charge explosive.

This finalized explosive composition, PBXC-125, consists of a simple two-component polyurethane binder system with 82% RDX. On degrading in a dilute ammonia solution, the polymerized binder breaks down to a diol and lysine, respectively—two non-polluting and harmless by-products. The main solids component (RDX) can be filtered, washed, dried, and then recycled, if necessary. The potential for this explosive's safe and rapid demilitarization was also demonstrated in a high-pressure water washout facility. Under the action of a high-pressure water jet, the cast explosive fill in a simulated warhead round was effectively removed in only a few seconds. Additional associated safety and sensitivity tests, performance tests, and thermal cookoff data will be described.

### **INTRODUCTION**

Military ordnance items containing high explosives are generally designed to withstand the rigors of rough handling and long-term storage, and to meet high reliability standards. However, if these ordnance items are not detonated as intended, they lose their effectiveness and reliability. Excessive aging, deterioration, or some other unanticipated event will then mandate that they be demilitarized and disposed of in an efficient, safe, and non-polluting manner.

Current air pollution abatement and environmental control regulations have imposed constraints on past methods of disposal and demilitarization of unserviceable ordnance explosives (References 1-3). An attractive alternative to continued open burning and demolition would be the development of a cast explosive whose main constituents could eventually be degraded and recycled into reusable explosive solids and liquid by-products which are environmentally non-hazardous. For several years the Naval Air Warfare Center Weapons Division, China Lake,

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Calif., has performed research and technology work concerned with the development of a castable plastic-bonded explosive composition that has the following characteristics:

1. Is water degradable at a good rate and produces no toxic degradation products.
2. Contains a binder that hydrolyzes and forms no high viscosity gels.
3. Contains a binder that does not degrade in the presence of water alone.
4. Contains an adequate explosive solids and energy output level.

This paper describes the efforts that went into accomplishing these objectives.

## APPROACH

Separation and recovery of ingredients from conventional high explosives are never simple and become particularly complex for plastic-bonded explosives. Such compositions contain a polymeric binder that has been reacted with a curative (cross-linking agent) to provide the mechanical strength necessary to maintain the explosive as a single coherent mass. To isolate the ingredients, the cross-linked polymer must be degraded to avoid the formation of viscous gels, which would inhibit the rate of degradation of the explosive. Although not recognized as being recyclable, the degraded polymeric binder should nevertheless yield only chemical species that are relatively innocuous. Excluding physical demilling operations, presently employed polymers for plastic-bonded explosives are not readily degraded.

Our approach, therefore, was to formulate exploratory, castable plastic-bonded explosives that would lend themselves to chemical degradation and separation of the binder from the solids fill. Moreover, to become competitive with existing Navy-approved high explosive compositions, our formulations had to pass the mandatory tests required by the Navy manual for interim qualification of explosives (Reference 4).

Emphasis was placed on using commercially available binder ingredients. Experience gained from working with solid propellant formulations was applied. Polyurethane binders that would undergo hydrolysis and breakdown by very dilute ammonia or acid solutions, but not by water (or moisture) alone, were initially selected. With HMX or RDX comprising the chief solids loading, plasticizers were added as needed to aid processing and casting. Problem areas in mixing and processing, curing, physical properties, explosive sensitivity, component compatibility, and thermal stability were addressed as they occurred.

The successful development of an explosive suitable for Navy qualification as a main charge explosive, but also environmentally safer, became a goal of this program.

## BINDER STUDIES AND EXPLOSIVES FORMULATIONS

### POLYURETHANES

Polyester and polyether diols readily yield processible formulations that cure with isocyanates to provide strong, flexible, elastomeric composite propellants and explosives. In view of the demonstrated compatibility and the availability of a variety of polyols and isocyanates, the polyurethane/isocyanate system was selected as the degradable binder to be used in the effort described herein.

RDX had demonstrated excellent compatibility with several polyurethanes in cast-cured explosives, and, at the time of this study, it was abundantly available in various classes. HMX, during this period, was reserved for other programs and was, thus, in limited supply.

Preliminary binder studies resulted in the selection of the first two candidates to be used in RDX formulations. The two candidates chosen were a hydroxyl-terminated polyester diol with a PEG adipate backbone (D22-45) and a hydroxyl-terminated polyether diol (L-35).

The high level of ether groups in D22-45 imparts flexibility and enhances the hydrophilic nature of the binder. The polyester also contributes to good processing and rheological properties. The urethanes formed from these polyester diols are capable of hydrolysis and degrade more readily than the polyether polyurethanes. Polyether diols such as L-35 are widely used as binders because of their excellent processing characteristics and their ability to impart elastomeric properties to cured compositions.

Since commercially prepared polyesters are not easily degraded, a curative that produces a urethane linkage capable of ammonolysis or hydrolysis was selected. In this case, it was LDIM. When cured with LDIM, urethane linkage degradation was found to be rapid and complete in dilute acid or ammonium hydroxide. However, when a hydrocarbon diisocyanate curative such as Hylene W was used, the binder showed little or no degradation after several weeks.

Various binder ingredients and combinations were tried in attempts to obtain the most suitable degradation characteristics. RDX fillers were added to the more promising binder formulations. Initial explosive formulations were then characterized as thoroughly as possible. Some of them are shown in the tables that follow.

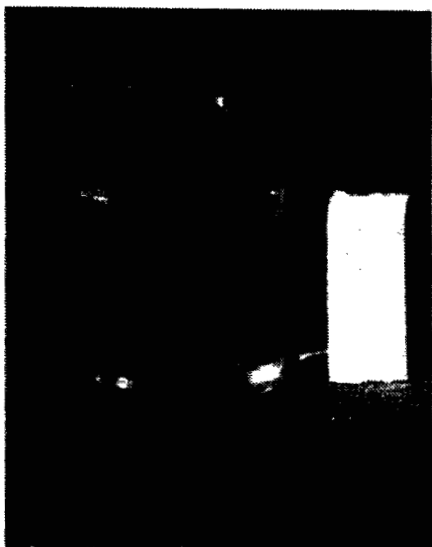
## EXPLOSIVE FORMULATIONS

Processing and mechanical properties were characterized, and minor refinements were made in the composition using the D22-45 polyester binder with the L-35 polyether diol. To aid in processing, as well as improving the aqueous ammonia degradation rate, triacetin was used as a plasticizer. The amount of triacetin ranged from 15 to 20% of binder. The RDX particle size distribution was revised to include some Class 2 size to improve rheology. Generally, the compositions were stable and exhibited no voids, gassing, or swelling under 60°C cure. Curing was completed in two days and yielded flexible compositions that were easily degraded by dilute aqueous ammonia and hydrochloric acid. Two early formulations, SBX-21 and SBX-23, are shown in Table 1.

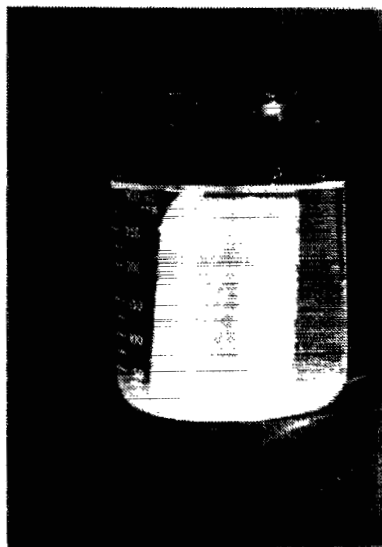
**TABLE 1. Formulations SBX-21 and SBX-23.**

Ingredient	Weight %	
	SBX-21	SBX-23
Binder <sup>a</sup>		
D22-45	6.89	5.51
L-35	6.73	8.11
LDIM	1.68	1.68
Triacetin	2.70	2.70
$\phi_3\text{Bi}$ (added)	(0.05)	(0.05)
RDX		
Class 1	15	15
Class 2	22	22
Class 3	15	15
Class 4	30	10
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	100	100
<sup>a</sup> NCO/OH equiv. ratio	1.10	1.10
L-35/D22-45 equiv. ratio	50/50	60/40

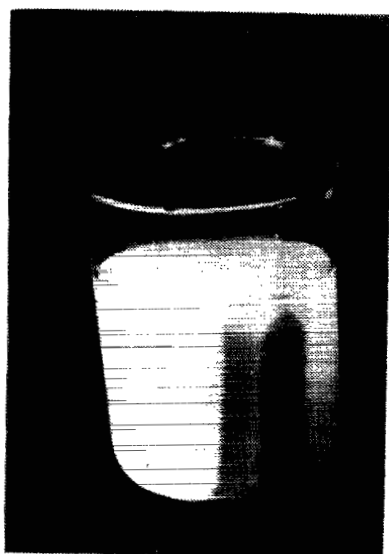
Binder-explosive breakdown occurs quite rapidly in dilute aqueous ammonia (5-7%), with the RDX settling out within 24 hours following submersion. This phenomenon is vividly demonstrated in Figures 1 through 4 (the explosive sample in this case is SBX-21). The solid precipitate (RDX) was easily filtered and separated from the clear liquid.



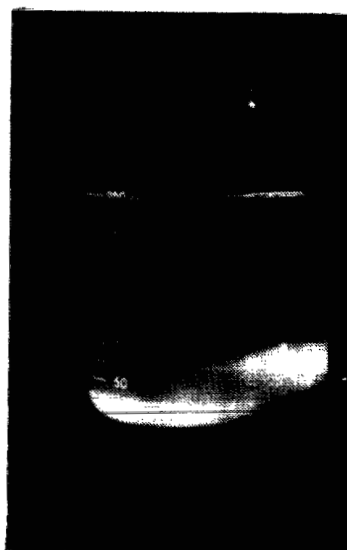
**FIGURE 1. Explosive Sample Before Immersion in Dilute Aqueous Ammonia.**



**FIGURE 2. Explosive Sample After a Few Minutes Immersion.**



**FIGURE 3. Explosive Sample After 1 Hour Immersion.**



**FIGURE 4. Explosive Sample After One Day Immersion.**

Because of the irregular nature of the RDX particles and the requirement to maintain a coarse RDX distribution to facilitate its recovery and recycling, the elongation values could not be improved. Binder NCO/OH and L-35/D22-45 equivalence ratios were varied, but no improvement in elongation was obtained. Further attempts to improve the mechanical properties met with little success because of the absence of a suitable bonding mechanism for the coarse RDX fillers at the 82% solids level. Several of the SBX formulations are discussed.

### Degradable Binder Explosive SBX-29

Formulation SBX-29 was prepared in a larger 3,000-gram batch size for additional data. Its composition and other properties are shown in Table 2.

**TABLE 2. SBX-29 Composition and Properties.**

Ingredient	Weight %
Binder	
D22-45	5.05
L-35	9.38
LDIM	1.77
Triacetin	1.80
ϕ <sub>3</sub> Bi (added)	(0.05)
(NCO/OH equiv. ratio = 1.10; L-35/D22-45 equiv. ratio = 65/35)	
RDX	
Class 1	
Class 2	82.00
Class 3	
Class 4	
Mechanical Properties	
Tensile strength, kPa (psi)	296 (43)
Elongation at max. stress, %	7
Elongation at rupture, %	9
Modulus, kPa (psi)	5937 (861)
Hazard Properties	
Impact sensitivity	28 cm (RDX = 14 cm)
Friction sensitivity	6/10 no fire at 4.448 kN (1,000 lb)
Electrostatic sensitivity	10/10 no fire at 0.25 J
Thermal Properties	
DTA	Onset of major exotherm, 190°C
TGA	Normal for RDX compositions
Physical Properties	
Shore A hardness	44
Measured density, g/cm <sup>3</sup>	1.539
End-of-mix viscosity (60°C), kPa-s	1.35

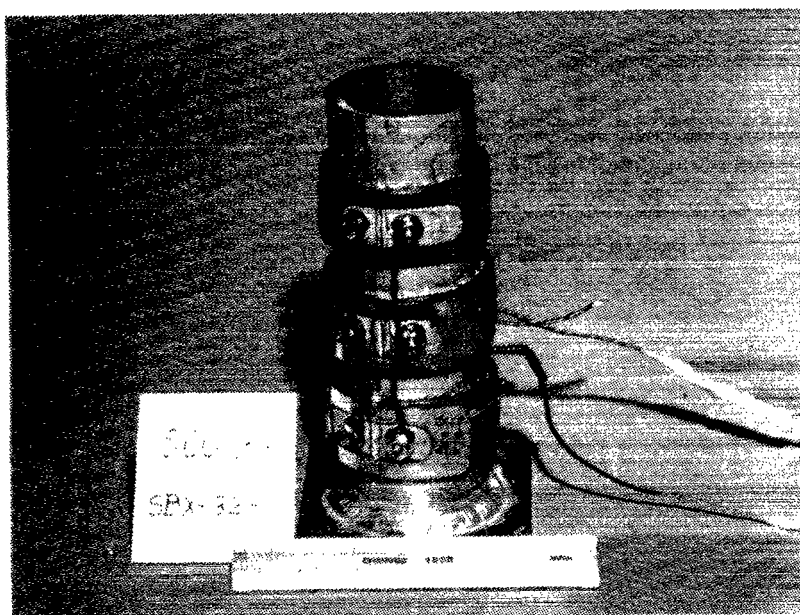
From this 3,000-gram mix of SBX-29, three units were cast for slow cookoff tests, in accordance with NAVORD OD 4481 (Reference 4). These tests are designed to determine the relative safety of the explosive material as it undergoes self-heating under varied conditions. For this type of tests, each sample is placed in an oven at a set temperature until the sample destroys itself (cooks off). For the purpose of this study, each sample consisted of a one-pint container instrumented with thermocouples and then filled with approximately 700 grams of the explosive.

During these tests, two samples, which were subjected to 130° and 140°C, liquefied and flowed away from the center-embedded thermocouple after the first exotherm peak had passed (at 28 hours and 13 hours, respectively). The third sample reacted normally by deflagrating within 7.5 hours at 200°C.

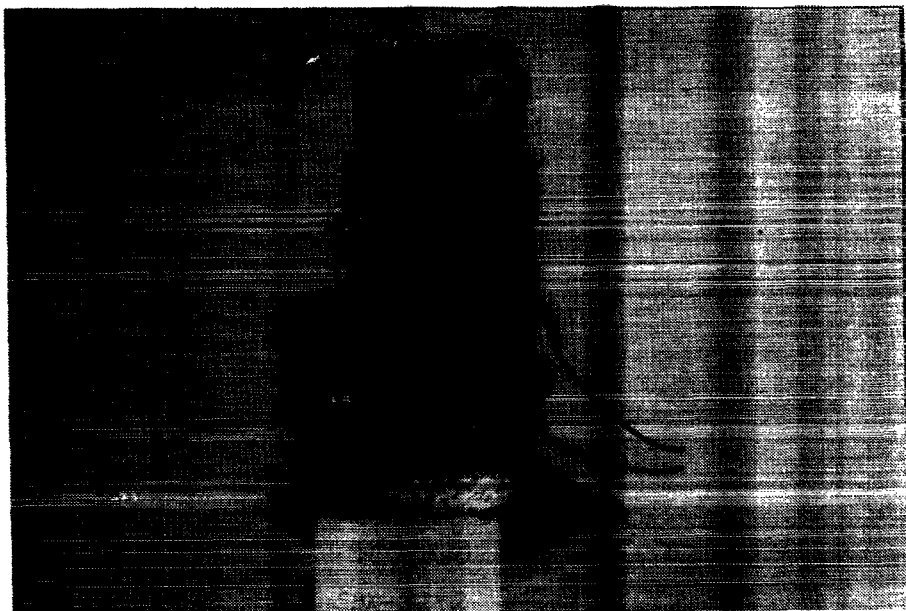


**TABLE 3. SBX-32 Composition and Properties.**

Ingredient	Weight %
Binder	
D22-45	5.61
L-35	10.42
LDIM	1.97
$\phi_3\text{Bi}$ (added)	(0.05)
(NCO/OH equiv. ratio = 1.0; L-35/D22-45 equiv. ratio = 65/35)	
RDX	
Class 1	
Class 2	82.00
Class 3	
Class 4	
Mechanical Properties	
Tensile strength, kPa (psi)	565 (82)
Elongation at max. stress, %	6
Elongation at rupture, %	7
Modulus, kPa (psi)	18,283 (2,652)
Hazard Properties	
Impact sensitivity	24 cm (RDX = 14 cm)
Friction sensitivity	6/10 no fire at 4.448 kN (1,000 lb)
Electrostatic sensitivity	10/10 no fire at 0.25 J
Physical Properties	
Shore A hardness	~55
Measured density, g/cm <sup>3</sup>	1.583
End-of-mix viscosity (60°C), kPa-s	1.10

**FIGURE 6. Results From First Slow Cookoff Run of SBX-32. Heating bands shown wrapped around circumference.**





**FIGURE 7. Results From Second Slow Cookoff Run of SBX-32.**

The time to reaction of SBX-32 at 139°C agrees well with the data reported earlier for SBX-29, after allowing for the cookoff sample size difference. With this qualitative agreement, the earlier estimate of a low characteristic "critical" temperature for thermal cookoff should stand. SBX-32 was then also dropped from further consideration.

#### **DEVELOPMENT OF CANDIDATE EXPLOSIVE SBX-34**

In an effort to further improve the thermal or cookoff behavior of a basic 82% RDX composition such as SBX-32, a simplified binder was adopted. Formrez YA 23-4, an adipate polyester with 79% polyethylene glycol content and a hydroxyl functionality of 2.33 (Witco Chemical Corp.) was chosen. This change would allow the elimination of the polyether diol L-35 from the binder, thus increasing the rate of degradation by ammonia-water.

One further step was taken. A finer RDX particle size in the solids blend was introduced in order to maintain adequate processing characteristics. This change resulted in formulation SBX-34. The end-of-mix viscosity was greatly improved over that of SBX-33. The composition and properties of SBX-33 and SBX-34 are shown in Table 4.

#### **SBX-34 SELF-HEATING SLOW COOKOFF TESTS**

SBX-34 was prepared in a 3,000-gram batch and cast into two heavy-walled aluminum tubes with approximately 260 grams of explosive in each. The tubes were then converted into slow cookoff vertical ovens, as for SBX-32, and heated. The results of the SBX-34 self-heating, slow cookoff tests are shown in Table 5.

**TABLE 4. Degradable Binder Explosives.**

Ingredient	Weight %	
	SBX-33	SBX-34
Binder		
YA 23-4	16.56	16.56
LDIM	1.44	1.44
$\phi_3\text{Bi}$ (added)	(0.05)	(0.05)
(NCO/OH equiv. ratio = 1.2)		
RDX		
Class 1	15	6.56
Class 2	22	—
Class 3	35	14.76
Class 4	10	38.54
Class 5	—	22.14
Mechanical Properties		
Tensile strength, kPa (psi)	614 (89)	552 (80)
Elongation at max. stress, %	3	3
Elongation at rupture, %	28	47
Modulus, kPa (psi)	28,159 (4,084)	27,187 (3,943)
Hazard Properties		
Impact sensitivity, cm	25	23
Friction sensitivity, kN (lb)	3,200 (724)	4,057 (912)
Electrostatic sensitivity, 0.25 J	10/10 no fire	10/10 no fire
VTS, mL/g/48hrs		0.03 (100°C) 0.75 (120°C)
Physical Properties		
Shore A hardness	66	63
Measured density, g/cm <sup>3</sup>	1,538	1,602
End-of-mix viscosity (55°C), kPa-s	2.5	1.2

**TABLE 5. SBX-34 Slow Cookoff Tests Results.**

Test No.	Oven Control Setting, °C	Observations
SCO-338	145	Explosive began foaming after 17.5 hours but no cookoff occurred. Test terminated after 19 hours.
SCO-339	165	Large 218-gram portion of explosive exuded out of oven during heating. Remainder cooked off (no detonation) in 4.5 hours.

From calculations derived from the tests, it was determined that SBX-34 had passed the requirements for self-heating, thermal stability, and slow cookoff. The calculation for the predicted critical temperature,  $T_m$ , was 124°C for a 12-inch-diameter warhead and 118°C for an 18-inch-diameter, 2,000-pound Mk 84 general purpose bomb.

## SBX-34 IN AIRCRAFT FUEL FIRE

In addition to being subjected to individual thermal test procedures and analyses, SBX-34 was also cast into an unlined, full-scale Zuni Mk 24 warhead and engulfed in a 750-gallon aircraft fuel fire. Temperatures reached 1094°C (~2,000°F) in just over a minute. Soon after, the Zuni round deflagrated and ruptured in essentially two large fragments. No small fragments were produced in this cookoff reaction. The fact that this round did not detonate was indeed a good indicator that this explosive formulation is a good candidate for use as an insensitive munition.

## EXPOSURE TO 100% RELATIVE HUMIDITY

What is the effect of long-term exposure to moisture on SBX-34? To answer this important question, three small samples of SBX-34 were placed in a covered glass desiccator containing ~300 mL of water. The desiccator was then placed in a steam oven set at ~52°C. The explosive samples were observed over a period of 8 days, and any physical dimensional change was noted. This exposure to 100% relative humidity was performed with the full realization that SBX-34 was an explosive composition with a water soluble and hydrolyzable binder. The results of the high humidity exposure test showed that the average weight percent gain after 3 days was 4.02%; after 8 days the average was 5.92%.

The 5-6% weight gain from moisture was expected. Surprisingly, however, the high moisture environment seemingly had very little effect on the physical strength of the samples. No slumping or other adverse effect on the samples was noted during the entire 8-day exposure period.

Three other solid cylindrical samples of SBX-34 (approximately 86 grams each, with density of 1.567 g/cm<sup>3</sup>) were subjected to the identical moisture environment for up to 22 days. After 10 days, physical dimensions and weights increased slightly with a corresponding drop in density.

After 22 days of 100% humidity exposure, the cylinders became more saturated and binder degradation more obvious. The samples were measured again. Weights had increased (more water absorbed) along with slight increases in volume. Weight gains averaged 3.82%. Density averaged 1.564 g/cm<sup>3</sup>—not much of a change from its original value.

It is encouraging to report that SBX-34, despite being a polyurethane-type explosive, will not easily undergo hydrolytic attack in the presence of moisture alone. Rather, it is designed to degrade *only* under controlled treatment with dilute ammonia or acid in explosives recovery.

The mechanism of binder degradation can be depicted by the chemical diagram shown in Figure 8.

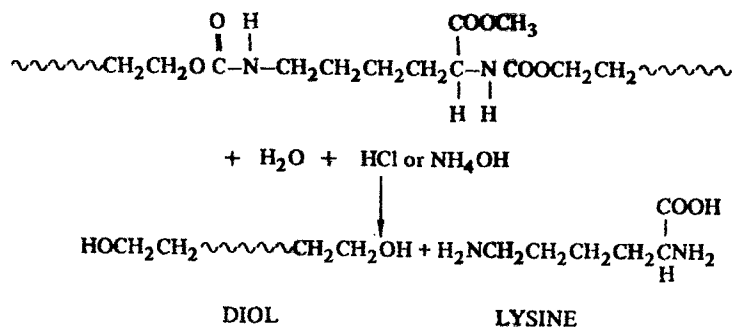


FIGURE 8. SBX-34 Polyurethane Binder.

The two products of binder breakdown, the diol and lysine, are considered safe and non-polluting, well within the scope and objective of this program.

## **BINDER DEGRADATION AND EXPLOSIVE RECOVERY**

Laboratory studies of RDX recovery from SBX-34 were also conducted with excellent results. Samples of SBX-34 (12.03, 12.41, and 6.50 grams) were immersed in ~50 mL of dilute (5%) ammonium hydroxide for a day, then rinsed, filtered, and dried overnight in a vacuum oven at 80°C. Results showed that the percentage of recovered RDX from each of the three samples equaled 82.46, 82.35, and 82.46%, respectively, (SBX-34 contains a total of 82% RDX in a blend of four classes). The fraction of a percent in excess weight might be attributed to adsorption of some residual binder on the RDX solids. It is quite conceivable that, in scale-up, the recovered blend of RDX could have been recycled to prepare another batch of explosive. The only other ingredients needed would have been the binder and curative. A cost advantage is definitely achievable.

Later, in a high-pressure water washout facility at another location, this explosive was effectively removed in only a few seconds from a simulated warhead round. Rapid and safe demilitarization was aptly demonstrated.

## **CONCLUSIONS**

The feasibility of composition SBX-34 in serving as an acceptable main charge explosive, yet contributing significantly to our nation's environmental pollution abatement efforts, was demonstrated. This investigation established that this composite polyurethane/RDX system, which is also easily degradable, can be used to formulate very adequate high explosives. Although some of the mandatory test requirements called for in NAVORD OD 44811 were not fulfilled in their entirety because of insufficient numbers of test samples, the values obtained from those limited tests were considered to be valid. Great efforts went into proving that this type of composition is relatively insensitive from the thermal standpoint. We believed that SBX-34 could be qualified as a main charge explosive for the Navy. So much so that SBX-34 was redesignated composition PBXC-125 at the termination of the program (References 6 and 7).

## **REFERENCES**

1. Executive Order 11507 of 4 February 1970. ". . . the Federal Government, in the design, operation, and maintenance of its facilities, shall provide leadership in the nationwide effort to protect and enhance the quality of our air and water resources."
2. OPNAVINST 6240.3E, 5 July 1977.
3. Executive Order 12088, "Federal Compliance With Pollution Control Standards," 13 October 1978.
4. Naval Ordnance Systems Command. *Safety and Performance Tests for Qualification of Explosives*, prepared by the Naval Weapons Center. Washington, D.C., NAVORD, 1 January 1972. (NAVORD OD44811, Volume 1, publication UNCLASSIFIED.)
5. Naval Weapons Center. *Thermal Analyses Studies on Candidate Solid JPL Propellants for Heat Sterilizable Motors*, by Jack M. Pakulak, Jr. and Edward Kuletz. China Lake, Calif., NWC, July 1970. (NWC TP 4258, publication UNCLASSIFIED.)

6. Naval Weapons Center. *Water Soluble and Hydrolyzable Binder Explosives*, by B.Y.S. Lee. China Lake, Calif., NWC, February 1982. (NWC TP 6313, publication UNCLASSIFIED.)

7. U. S. Patent No. 4,293,352. *Degradable Binder Explosives*, by Benjamin Y. S. Lee, Russel Reed, Jr., and Roger L. Miller, 6 October 1981.

## GLOSSARY

D22-45	Hydroxyl-terminated polyester diol with a polyethylene glycol adipate backbone; $f \approx 3$ (Witco Chemical Corp.)
DTA	Differential thermal analysis
f	Functionality
HMX	Cyclotetramethylenetetranitramine
Hylene W	4,4'-diisocyanatodicyclohexyldiphenylmethane (E. I. duPont de Nemours and Co.)
L-35	Diol, 50% ethylene oxide-capped polyoxypropylene glycol (BASF Wyandotte Corp.)
LDIM	Lysine diisocyanate methyl ester (Dexter Midland Corp., Toray Industries)
NCO	Isocyanate
OH	Hydroxyl
PBX	Plastic-bonded explosive
PEG	Polyethylene glycol
RDX	Cyclotrimethylenetrinitramine
SBX	Soluble binder explosives (denotes series assigned to formulations in this program)
TGA	Thermogravimetric analysis
VTs	Vacuum thermal stability
$\phi_3\text{Bi}$	Triphenylbismuth
YA 23-4	Adipate polyester with 79% polyethylene glycol content, hydroxyl $f = 2.33$ (Witco Chem. Corp.)